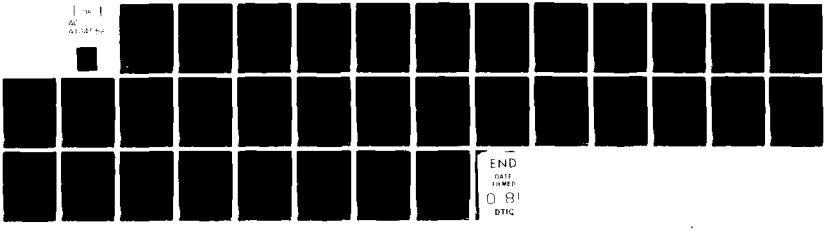
AD-A104 556 MCDONNELL AIRCRAFT CO ST LOUIS MO F/G 11/1
CHEMORHEOLOGY AND QUALITY CONTROL FOR AN ADHESIVE.(U)
JUL 81 J F CARPENTER N00019-80-C-0319
UNCLASSIFIED NL



AD A104556

CHEMORHEOLOGY AND QUALITY CONTROL FOR AN ADHESIVE

McDonnell Aircraft Company
McDonnell Douglas Corporation
P.O. Box 516
St. Louis, Missouri 63166

J.F. Carpenter

July 1981

Technical Report N00019-80-C-0319
Final Report for Period 15 July 1980 - 15 July 1981

Distribution unlimited

Department of the Navy
Naval Air Systems Command
Code AIR-52032C
Washington, D.C. 20361

APPROVED FOR PUBLIC RELEASE:
DISTRIBUTION UNLIMITED

DTIC FILE COPY

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE *(When Data Entered)*

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER N00019-80-C-0319	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE *(and Subtitle)* CHEMORHEOLOGY AND QUALITY CONTROL FOR AN ADHESIVE.		5. TYPE OF REPORT & PERIOD COVERED Final Report. ~~for Period~~ 15 July 80 — 15 July 81 6. ~~PERFORMING ORG.~~ REPORT NUMBER
7. AUTHOR(s) J. F. Carpenter		8. CONTRACT OR GRANT NUMBER(s) N00019-80-C-0319
9. PERFORMING ORGANIZATION NAME AND ADDRESS McDonnell Aircraft Company McDonnell Douglas Corporation P. O. Box 516, St. Louis, MO 63166		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS Department of the Navy Naval Air Systems Command Washington, D. C. 20361 Code: AIR-5163		12. REPORT DATE July 1981 13. ~~NUMBER OF~~ PAGES 23
14. MONITORING AGENCY NAME & ADDRESS *(if different from Controlling Office)*		15. SECURITY CLASS. *(of this report)* Unclassified 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT *(of this Report)*

APPROVED FOR PUBLIC RELEASE.
DISTRIBUTION UNLIMITED

17. DISTRIBUTION STATEMENT *(of the abstract entered in Block 20, if different from Report)*

Approved for public release; distribution unlimited

18. SUPPLEMENTARY NOTES

19. KEY WORDS *(Continue on reverse side if necessary and identify by block number)*

Physicochemical Characterization
Quality Assurance
Reliability Aircraft Adhesive
Rheology of Resins

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

The objective of this program has been to develop rheological test methods applicable to an adhesive system and demonstrate the viability of these techniques for in-plant quality control and to establish acceptance criteria with statistically valid accept/reject limits.

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE *(When Data Entered)*

4 0 3 1 1

FOREWORD

This final report covers work performed under Contract No. N00019-80-C-0319 from 15 July 1980 to 15 July 1981. Work was performed by the Material and Process Development Department of the McDonnell Aircraft Company, McDonnell Douglas Corporation, St. Louis, Missouri. The program was administered under the direction of Naval Air Systems Command by Mr. John Gurtowski.

The program was managed by Mr. R. J. Juergens, with Dr. J. F. Carpenter as Principal Investigator. Major contributors were Messrs. T. T. Bartels, W. D. Tims, F. W. Giblin, C. E. Wilson, G. Blase, M. E. Smith, J. Twitchell, and W. J. Keyes of the Materials Laboratory.

For the purpose of this report, certain resin components are identified by code designations, rather than by trade or chemical names.

TABLE OF CONTENTS

PRECEDING PAGE BLANK-NOT FILMED

LIST OF ILLUSTRATIONS

LIST OF TABLES

LIST OF ABBREVIATIONS

RDS	Rheometrics Dynamic Spectrometer
HPLC	High Performance Liquid Chromatography
IR	Infrared Spectroscopy
GC	Gas Chromatography
GPC	Gel Permeation Chromatography
DSC	Differential Scanning Calorimetry
RT	Room Temperature
ET	Elevated Temperature
T_{gel}	Temperature at Gel
T_g	Glass Transition Temperature
T_{os}	Reaction Onset Temperature
T_{exo}	Reaction Exotherm Temperature
T_{cr}	Complete Reaction Temperature
η	Viscosity
t_{gel}	Time to Gel
G'	Storage Modulus
G"	Loss Modulus
ΔH	Enthalpy
ω	Dynamic Frequency
γ	Strain
$\dot{\gamma}$	Rate of Strain
Φ	Linear Heating Rate
FTIR	Fourier Transform Infrared
RPLLC	Reverse Phase Liquid Chromatography
g	Gram
ml	Milliliters
r^2	Correlation Coefficient
KF	Karl Fischer (water test)
SLS	Single Lap Shear
DLS	Double Lap Shear
FWT	Flatwise Tension
S_x	Standard Deviation

1.0 INTRODUCTION & SUMMARY

Adhesively bonded structures for aircraft are manufactured from many lots of film adhesive over an extended time span. It is important that these materials have consistent flow properties to ensure the reliability, reproducibility, and durability of the bonded structures. Both the material supplier and the fabricator must therefore implement adequate quality control of the flow properties of the adhesive materials. Most adhesive resin systems used in structural applications are chemically complex. An undetected formulation or processing error in the manufacture of the resin system system can have a serious effect on the structural and environmental integrity of flight hardware fabricated with this anomalous material.

While performance type quality control tests have served acceptably in the past and physiochemical tests are being introduced, additional quality assurance tests are necessary to ensure rheological (flow) consistency.

Thus the objectives of this program were to develop rheological test methods applicable to the adhesive system, to demonstrate the viability of these techniques for in-plant quality control, and finally to establish acceptance criteria with statistically valid accept/reject limits.

These objectives were met. The viability of the rheological test method was demonstrated by good correlation with the chemical and thermal properties of intentionally altered batches. Replicate testing of multiple production batches showed good method precision; however, batch-to-batch variation of current vendor material was too great to establish meaningful accept/reject limits.

2.0 PROGRAM PLAN

The technical approach used is given in the Program Plan, Figure 1. A suitable test method was selected and optimized. The viability of the optimized method was demonstrated by measuring the flow characteristics of altered baseline materials. Alterations included changes in moisture content and level of advancement (B-stage) of the as-received adhesive. Other than a change in the starting chemical composition, moisture content and degree of advancement were considered to be the two most likely variations in as-received material to affect the rheology of the adhesive. Under fixed cure cycle conditions any changes in resin flow of the adhesive may adversely affect the mechanical properties of the bond.

Selected physiochemical and mechanical property tests were made to determine correlative relationships with changes in the rheology of altered baseline adhesive. Finally, five production batches each of Types I and II adhesive were tested in replicate for rheological properties by the optimized test method to establish statistically valid acceptance limits.

PHASE I - ESTABLISH VISCOELASTIC PROPERTIES AND TEST METHOD

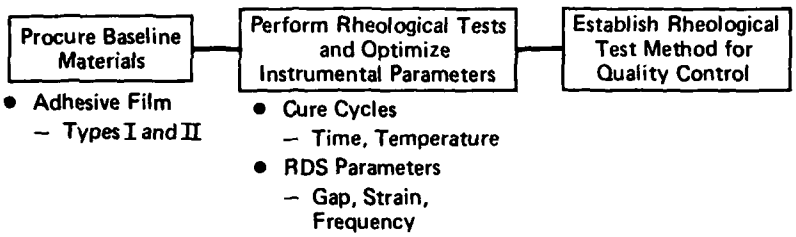
The objective of this phase was to establish a suitable rheological test method for quality control of an adhesive. The RDS-7700 rheometrics dynamic spectrometer was the instrument of choice. The objective was accomplished by first measuring viscosity profiles of the baseline materials under varied cure cycle conditions to determine the best time/temperature combination. The selected cure cycle was then used to optimize the instrumental test parameters for the rheometer.

Preliminary in-house cure cycle investigations indicated that viscoelastic measurements made using linear heating rates gave more reproducible viscosity profiles than measurements made under various isothermal hold conditions. Viscosity measurements for the baseline material were made using linear heating rates of 1°C, 2°C, and 4°C/minute. The selected heating rate of 2°C/min was then used for a series of measurements to establish the optimum instrumental parameters of strain, frequency and starting temperature.

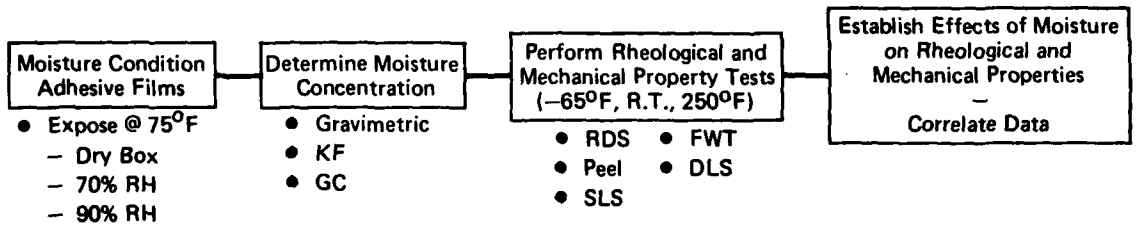
PHASE II - DETERMINE EFFECT OF MOISTURE ON MECHANICAL PROPERTIES AND CORRELATE WITH RHEOLOGY

In this phase, specimens with varied moisture content were tested for rheological properties, using the optimized test method developed in Phase I. Mechanical test specimens were prepared from moisture-conditioned adhesive films and tested at

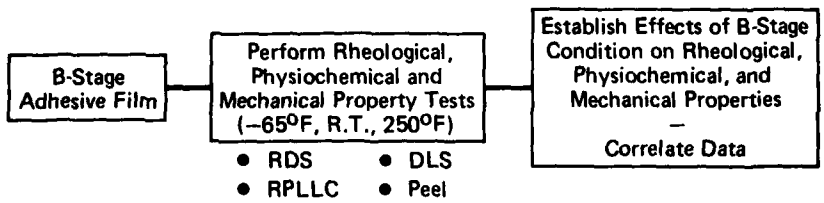
Phase I - Establish Viscoelastic Properties and Test Methods



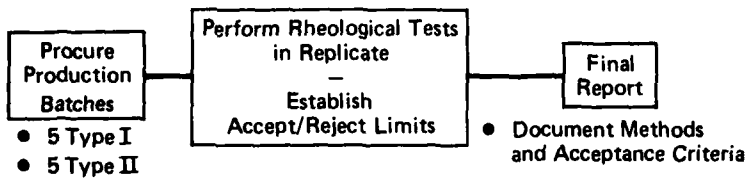
Phase II - Determine Effects of Moisture on Mechanical Properties and Correlate with Rheology



Phase III - Determine Effects of B-Staging on Mechanical and Physiochemical Properties and Correlate with Rheology



Phase IV - Establish Receiving Inspection Controls for System Rheology



GP13-0422-14

Figure 1. Program Plan Chemorheology and Quality Control for an Adhesive

three different temperatures. The effects of various moisture contents on rheological properties were compared with their effects on mechanical properties.

The adhesive is supplied as Type I and Type II. The two types have the same chemistry but differ in the weight percent scrim and in scrim weave. In addition, Type I is supplied at a nominal film weight of 0.1 lb/ft^2 and Type II is a nominal 0.08 lb/ft^2.

The moisture content of adhesive films, Types I and II was varied by drying the as-received material to constant weight over a commercial desiccant (Drierite) and by exposing the as-received material to constant weight (equilibrium) at 70% RH and 90% RH. All exposures were made at 75°F. The moisture content of the specimens was measured by three methods: gas chromatography, Karl Fischer titriation, and weight gain or loss.

PHASE III - DETERMINE EFFECTS OF B-STAGING ON MECHANICAL AND PHYSIOCHEMICAL PROPERTIES AND CORRELATE WITH RHEOLOGY

The objective of this phase was to determine the effects of B-Staging (advancement) of the adhesive on its mechanical, physiochemical and rheological properties. The vendor B-stages the material to a certain level of advancement during formulation.

For this phase, the as-received Type I adhesive was given additional in-house B-staging of 0.5 and 1.0 hour at 240°F. The as-received Type II adhesive was B-staged in-house for 1.0, 2.0 and 3.0 hours at 240°F. All B-staged specimens were tested for rheological properties. The Type II B-staged specimens were also tested for any changes in physiochemical and mechanical properties.

PHASE IV - ESTABLISH RECEIVING INSPECTION CONTROLS FOR SYSTEM RHEOLOGY

In this phase, five recent production batches of Types I and II adhesive were tested in replicate for rheological properties and thermal characteristics. The test matrices were used to determine acceptance limits based on encompassing 99% of the expected variation at 95% confidence limits.

3.0 TECHNICAL RESULTS

3.1 PHASE I - ESTABLISH VISCOELASTIC PROPERTIES AND TEST METHODS - The rheometrics dynamic spectrometer (RDS) Model 7700, was the instrument selected for this program. It is a dynamic, oscillatory rheometer capable of measuring rheology over a wide range of temperatures and can be programmed for any combination of linear heating rates, isothermal holds, and simulated cure cycle conditions. It provides continuous printout of data and automatically plots dynamic viscosity (η), loss modulus (G") and storage modulus (G'). In addition, in the plate-to-plate mode, measurements can be made on the as-received adhesive without removing the scrim.

3.1.1 Selection of Cure Cycle Conditions - From in-house investigations, it was determined that the RDS data most useful for quality control purposes was obtained from viscosity profiles (plots of viscosity vs. time) for selected cure cycles. It was further determined that flow measurements made using linear heating rates to the gel point were more reproducible than measurements made under isothermal hold conditions. Therefore, the first step in optimizing the test method for quality control purposes was to measure viscosity as a function of time for linear heating rates of 1°C, 2°C, and 4°C/min. The following nominal set of instrumental parameters, currently used for receiving inspection, were used for these determinations:

- Plate gap = 3 plies of adhesive (specimen thickness)
  - 1.1 mm for the Type I Adhesive
  - 0.85 mm for the Type II Adhesive
- Frequency = 10 rad/sec
- Time span = t_o to t_{gel}
- Strain = 20%

Test data are given in Table 1. Duplicate viscosity profiles produced at 2°C/min and 4°C/min were more reproducible, and required less test time than the determinations at 1°C/min. Since more literature data is being reported at 2°C/min than at 4°C/min, the former heating rate was chosen.

3.1.2 Selection of RDS Instrumental Parameters - Strain and frequency sweep were then made at 50°C and additional viscosity profiles were generated at different frequencies and different percentages of strain. The instrumental settings selected for rheological quality control tests are as follows:

- Starting Conditions: 3 ply thickness, 60°C
- Frequency: 20 rads/sec
- Strain: 50%
- Heating Rate: 2°C/min

TABLE 1. RHEOMETRICS DATA AT THREE LINEAR HEATING RATES FOR ADHESIVE (TYPES I AND II)

Material	Heating Rate (°C/min)	Viscosity, η Minimum (Poise x 10^2)	Time to Gel (min)
Adhesive (Type I)	1	3.8 (3.5, 4.0)	107 (106, 108)
	2	2.6 (2.5, 2.7)	60.5 (61, 60)
	4	2.5 (2.5, 2.5)	35 (35, 35)
Adhesive (Type II)	1	3.9 (3.5, 4.3)	104 (104, 104)
	2	3.4 (3.7, 3.1)	58 (58, 58)
	4	2.0 (1.6, 2.4)	35 (35, 35)

GP13-0422-2

These conditions were selected to improve the signal to noise ratio obtained at minimum viscosities, and thus improve the test precision. For example, at 1 rad/sec frequency and 20% strain, the torque values at minimum viscosity ranged from 0.6 to 1.3 gm-cm. Increasing the frequency to 10 rads/sec at the same strain gave somewhat higher torque values of 1.5-2.5 gm-cm. However, these values still gave poor sensitivity, since they are at the lower extreme of the linear range for the 2000 gm-cm torque transducer now installed in the RDS 7700 instrument.

We increased the strain to 90% for 1 rad/sec frequency and obtained minimum values of about 5 gm-cm. Extrapolation of these findings lead to the selection of 20 rads/sec frequency at 50% strain as test parameters. This combination avoids an overload (> 2000 gm-cm) at the high viscosity end of the curve while bringing the torque at the minimum viscosity to about 10 gm-cm. The starting temperature for the optimized parameters was raised from 50°C, used in the early runs, to 60°C. The higher starting temperature lowered the starting viscosity and provided the adhesion needed to avoid plate-to-sample slippage under the increased strain.

Figure 2 compares the viscosity profiles generated under current receiving inspection parameters with the optimized parameters developed in this program. With the optimized method there was much less data scatter, particularly in the lower viscosity area, where the greater part of the flow takes place.

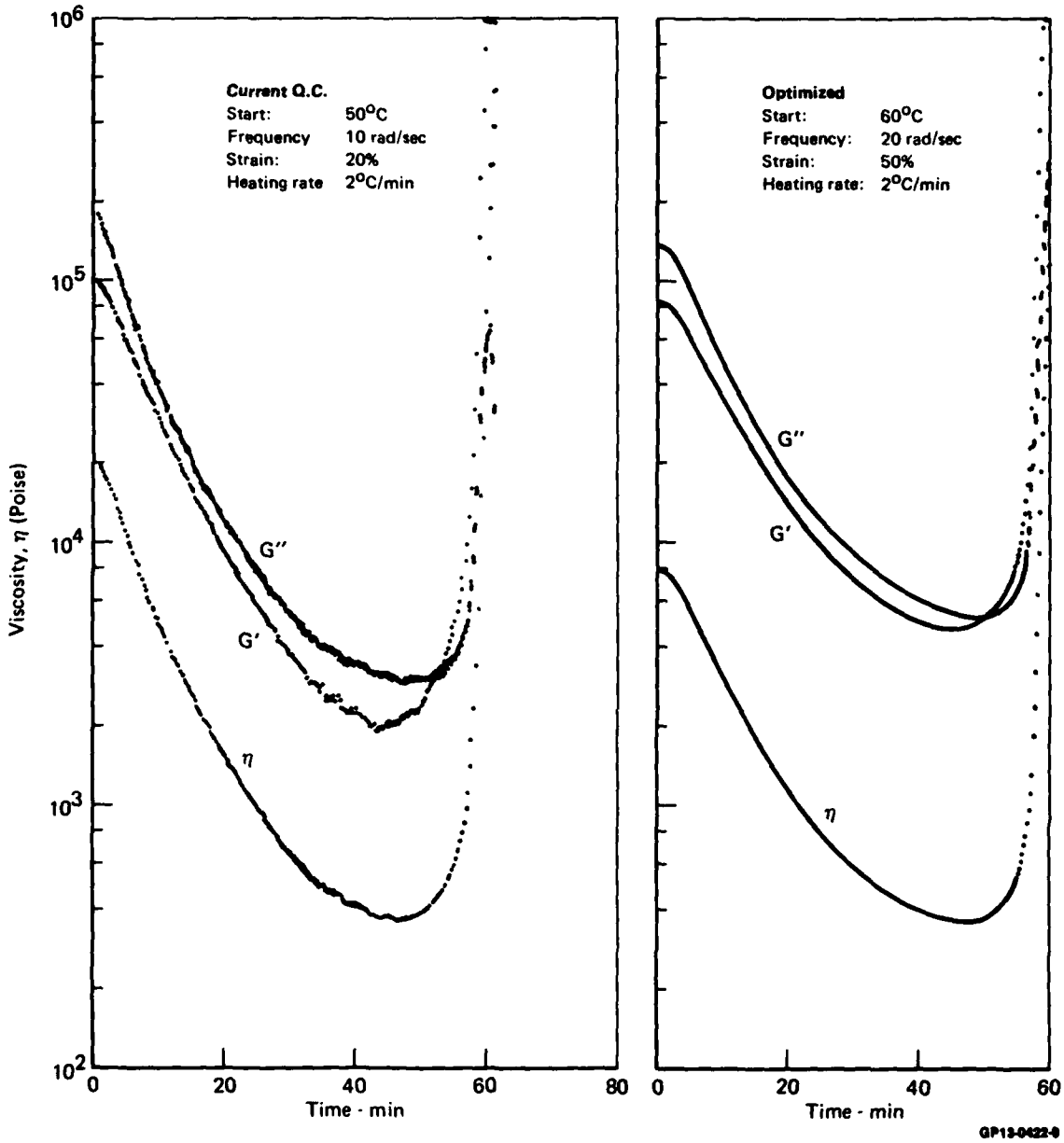


Figure 2. Optimization of Rheometrics Test Parameters for Adhesive Viscosity Profiles

3.2 PHASE II - DETERMINE EFFECTS OF MOISTURE ON MECHANICAL PROPERTIES AND CORRELATE WITH RHEOLOGY

3.2.1 Moisture Conditioning of Adhesive Films - To achieve specimens of adhesives having varied moisture content, one set each of the as-received Type I and Type II adhesive was dried over a commercial desiccant (Drierite) to constant weight and two other sets were exposed in humidity cabinets to constant weight (equilibrium) at 70% RH and 90% RH. All exposures were at 75°F. Since single plies of adhesive films were exposed, most of the weight gain at high humidity took place in the first few hours of exposure. Traveler specimens 4 x 4 inches were used to monitor weight gain or loss. After reaching equilibrium, the moisture content of the exposed adhesive films was measured by gas chromatography and by the Karl Fischer titrimetric method. While the change in moisture concentration was suitably monitored by the weight change of the traveler specimens, the weight change was too small to obtain good quantitative data. It was noted, however, that no significant weight loss was obtained for the as-received specimens exposed over Drierite. Unfortunately, the Karl Fischer results were not accurate due to deposition of the resin on the electrode. Gas chromatography (GC) measurements were reproducible and presumed accurate. The values for water content are given in Table 2. The weight percent scrim was determined for each specimen and water content is expressed both

TABLE 2. WATER CONTENT OF DRIED AND HUMIDITY EXPOSED SPECIMENS FOR ADHESIVE (TYPES I AND II)

Material	Exposure Condition	Water Content (wt %)		
		Gas Chromatography		Scrim (wt %)
		Film Basis	Resin Basis	
Adhesive (Type I)	Dried @ 75°F (M_0)	0.21 (1)	0.25	8.2
	As-Received (M_1)	0.18 (1)	0.19	8.2
	70% RH @ 75°F (M_2)	0.39	0.42	8.2
	90% RH @ 75° (M_3)	0.47	0.51	8.3
Adhesive (Type II)	Dried @ 75°F (M_0)	0.31 (1)	0.32	3.4
	As-Received (M_1)	0.20 (1)	0.21	3.4
	70% RH @ 75°F (M_2)	0.33	0.34	3.6
	90% RH @ 75°F (M_3)	0.47	0.48	3.5

Note:
(1) Moisture content for dried specimen appears high - explanation is given in text

GP13-0422-3

on total film basis and on weight percent of resin basis. The moisture determinations were made on the traveler specimens used to monitor exposure, except for the as-received specimen. The as-received specimen was taken from a different location on the same roll of material and actually showed a slightly lower moisture concentration than the dried material.

3.2.2 Determination of Moisture Effects on Rheological Properties - The rheograms obtained using the optimized parameters for the RDS-7700 were used to check the effects of moisture on the rheology of Type I and Type II adhesive. In the instrumental optimization tests, data scatter and minimum viscosity values were satisfactory for comparative purposes. For subsequent testing, the rheograms obtained were also evaluated on the basis of "flow numbers".

The calculation of the flow number is based on the fact that total flow is directly related to the time of flow and inversely related to viscosity (η). Thus, a quantitative measure of total flow can be obtained by integrating dt/η from the start of the cure cycle at time (t_o) through the time of gel (t_{gel}). It would appear possible to use either the minimum viscosity or the flow number value for routine receiving inspection; however, the flow number values include the entire viscosity profile and are more meaningful from the standpoint of processing behavior.

Table 3 lists the results obtained for the rheological properties of specimens with variations in moisture content. For the Type I adhesive, the flow numbers indicate a trend toward a slight drop in flow with increased moisture content. No significant change was noted for the Type II adhesive.

TABLE 3. EFFECT OF MOISTURE ON RHEOLOGY FOR ADHESIVE (TYPES I AND II)

Material	Exposure Condition	Water[1] (wt %)	RDS-Flow Number (min/Poise) x 10^{-2}	Viscosity, η Minimum (Poise) x 10^{2}
Adhesive (Type I)	M_o	0.21	10.11 (9.508, 10.710)	2.57 (2.712, 2.432)
	M_1	0.21	9.99 (9.698, 10.280)	2.57 (2.632, 2.504)
	M_2	0.42	9.11 (9.208, 9.012)	2.76 (2.742, 2.785)
	M_3	0.51	9.02 (9.423, 8.611)	2.82 (2.766, 2.869)
Adhesive (Type II)	M_o	0.26	8.74 (8.113, 9.367)	3.12 (3.250, 2.990)
	M_1	0.26	8.78 (8.691, 8.878)	3.14 (3.186, 3.100)
	M_2	0.34	8.76 (8.389, 9.129)	3.14 (3.294, 2.976)
	M_3	0.48	8.45 (8.763, 8.134)	3.26 (3.183, 3.335)

GP13-0422-4

Note:
(1) Resin basis

3.2.3 Determination of Moisture Effects on Mechanical Properties - The Type I moisture conditioned adhesive materials were used to prepare mechanical test specimens. Single lap shear, Bell peel, and flatwise tension specimens were fabricated from adhesives at each moisture level and tested at temperatures of -65°F, RT, and 250°F. Test specimens were prepared as follows:

Single Lap Shear Tests - Thin sheet (0.063 in.) 7075-T6 bare aluminum was used for bonding the adhesive. Prior to priming, each aluminum panel was vapor degreased, then treated with alkaline cleaner followed by acid etch. American Cyanamid BR127 primer was used to prime aluminum surfaces. The specimens were cured at 350°F for 60 minutes. Autoclave pressure, heat up rates, post cure time, etc., routinely used for receiving inspection tests were used for specimen fabrication.

Bell Peel Tests - Cleaning and priming operations similar to those used for fabrication of lap shear specimens were used to prepare 2024-T3 aluminum for bonding. The adhesive was bonded between prepared aluminum sheets under fixed cure cycle conditions.

Flatwise Tension Tests - Specimens were fabricated using thin sheet 7075-T6 bare aluminum and 5056-H-39 non-perforated aluminum honeycomb core. Bonding surfaces were vapor degreased, alkaline cleaned and primed with BR127 primer. Adhesive strength was measured by loading the face to core bond in tension at a rate of 900-1000 pounds per minute until failure.

The data for Type I adhesive are given in Table 4. The average of the Bell peel test results for Type I adhesive show a slight trend toward an increase in peel for increased moisture content. Conversely, the single lap shear values at room temperature and 250°F test temperatures and the flatwise tension at 250°F show a slight decrease.

The Type II moisture conditioned adhesive was used to prepare Bell peel and double lap shear (DLS) mechanical test specimens. The double lap shear specimens were prepared by cocuring five plies of AS/3501-6 graphite epoxy to 0.05 inch 6-4 titanium. The mechanical properties measured at three test temperatures are given in Table 5. The Bell peel test results at room temperature and 250°F show a trend toward slightly greater values with an increase in moisture content of the adhesive. The double lap shear results show a trend toward a slight drop in values obtained at the 250°F test temperature with an increase in moisture content of the adhesive.

TABLE 4. EFFECT OF MOISTURE ON MECHANICAL PROPERTIES FOR ADHESIVE, TYPE I

Bell Peel

Exposure Condition @ 75°F	Moisture (wt%)	Bell Peel (lb/in.)[1]		
		−65°F	R.T.	250°F
M_0 (Dried)	0.20	8.2	29.0	27.4
S_x[2]		(3.5)	(1.7)	(5.5)
M_1 (As-Received)	0.20	9.8	30.2	27.9
S_x		(4.0)	(2.7)	(4.0)
M_2 (70% RH)	0.39	19.8	31.5	31.0
S_x		(4.5)	(4.2)	(5.9)
M_3 (90% RH)	0.47	10.8	33.6	32.9
S_x		(8.8)	(5.6)	(6.3)

Single Lap Shear

Exposure Condition @ 75°F	Moisture (wt%)	Single Lap Shear (psi)[1]		
		−65°F	R.T.	250°F
M_0 (Dried)	0.20	3,690	4,640	3,120
S_x		(900)	(470)	(315)
M_1 (As-Received)	0.20	4,430	4,920	3,390
S_x		(465)	(160)	(185)
M_2 (70% RH)	0.39	3,510	3,650	3,700
S_x		(215)	(370)	(145)
M_3 (90% RH)	0.47	3,730	3,960	3,450
S_x		(575)	(340)	(130)

Flatwise Tension

Exposure Condition @ 75°F	Moisture (wt%)	Flatwise Tension (psi)[1]		
		−65°F	R.T.	250°F
M_0 (Dried)	0.20	1,560	1,510	980
S_x		(40)	(90)	(70)
M_1 (As-Received)	0.20	1,640	1,560	1,010
S_x		(40)	(135)	(80)
M_2 (70% RH)	0.39	1,600	1,530	920
S_x		(80)	(60)	(35)
M_3 (90% RH)	0.47	1,450	1,420	950
S_x		(135)	(80)	(85)

(1) Average of 5 values
(2) S_x = standard deviation

GP13-0422-16

TABLE 5. EFFECT OF MOISTURE ON MECHANICAL PROPERTIES FOR ADHESIVE, TYPE II

Bell Peel

Exposure Condition @ 75°C	Moisture (wt%)	Bell Peel (lb/in.)(1)		
		−65°F	R.T.	250°F
M_0 (Dried)	0.25	3.5	26.9	41.9
S_x(2)		(1.0)	(3.3)	(2.1)
M_1 (As-Received)	0.25	3.5	32.5	40.0
S_x		(1.0)	(1.2)	(2.8)
M_2 (70% RH)	0.33	3.0	34.8	43.6
S_x		(0.7)	(0.8)	(1.4)
M_3 (90% RH)	0.47	3.8	37.0	45.5
S_x		(0.0)	(1.0)	(2.4)

Double Lap Shear

Exposure Condition @ 75°F	Moisture (wt%)	Failing Stress (psi)(1)		
		−65°F	R.T.	250°F
M_0 (Dried)	0.25	4,600	4,480	2,300
S_x		(490)	(200)	(85)
M_1 (As-Received)	0.25	4,440	4,340	2,390
S_x		(400)	(290)	(140)
M_2 (70% RH)	0.33	4,260	4,020	2,140
S_x		(540)	(140)	(210)
M_3 (90% RH)	0.47	4,800	4,910	2,140
S_x		(240)	(120)	(185)

(1) Average of 5 valves
(2) S_x = standard deviation

GP13-0422-17

3.2.4 Correlation of Rheological and Mechanical Property Data for Variations in Moisture Content - The rheological and mechanical data for both Types I and II adhesive show that the moisture content of the adhesive had no statistically significant effect on either of these properties. The double lap shear values for Type II adhesive are lower than the current receiving inspection value. This was probably due in part to the fact that the probable loss of moisture did not allow the adhesive to be B-staged on the titanium metal. The reason for low values for Bell peel strength at -65°F for both types of adhesive is unknown.

3.3 PHASE III - DETERMINE EFFECTS OF B-STAGING ON MECHANICAL AND PHYSIOCHEMICAL PROPERTIES AND CORRELATE WITH RHEOLOGY

3.3.1 Preparation and Rheological Determinations for the B-Staged Specimens - Type II adhesive film was staged for 1, 2, and 3 hours at 240°F. Type I film was staged at the same temperature for 0.5 and 1.0 hours. The as-received and staged materials for both Types I and II were tested for rheological properties. The Type II specimens were also tested for physiochemical and mechanical properties.

Rheological Properties - The rheograms obtained using the optimized instrumental parameters clearly showed the effects of B-staging on both Type I and Type II. Figure 3 shows the viscosity profiles obtained for Type II, as-received and after additional in-house B-staging. The viscosity is higher for the

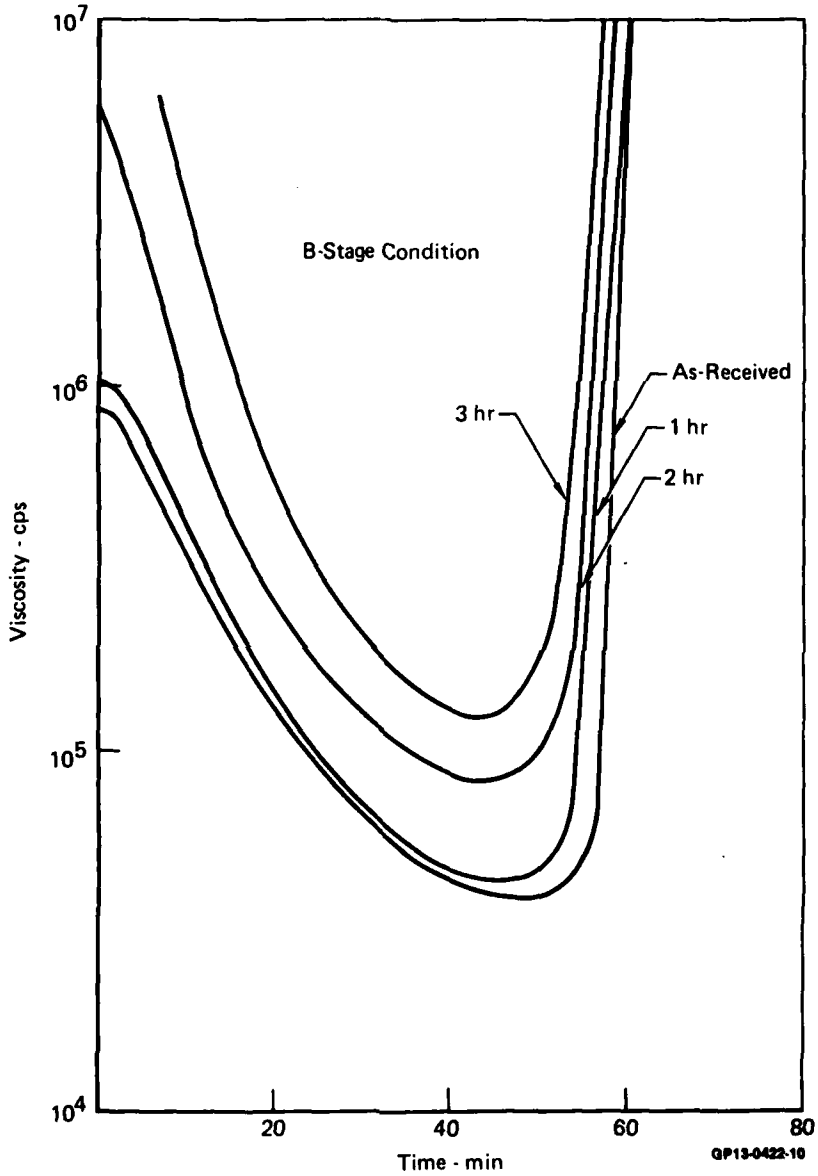


Figure 3. Effect of B-Staging on Viscosity Profile for Adhesive @ 2°C/min

staged materials throughout the cycle and the time to gel is decreased. Thus, the total flow of the resin decreases as B-staging is increased. Critical data obtained from the viscosity profiles for these materials are given in Table 6.

3.3.2 Physiochemical Characterization of B-staged Specimens - The physiochemical tests selected to measure the effects of B-staging were liquid chromatography and differential scanning calorimetry.

Characterization by Liquid Chromatography - Reverse phase gradient liquid-liquid chromatography (RPLLC) separates the resin components on the basis of differences in their polarity. By RPLLC it is possible to measure the relative amounts of unreacted (free) components and the reaction products formed during vendor formulation of the resin. Figure 4 shows the chromatogram of the as-received Type II adhesive batch. The peaks are identified in Figure 5.

To determine the effects of additional B-staging on the adhesive, each peak area was ratioed to a single peak. It was evident that measurement of uncombined curing agent No. 2 gave the best correlation with the degree of resin advancement obtained by additional in-house B-staging. Standards made up having known amounts of free curing agent No. 2 were used to calculate the weight percent of this component. The data is given in Table 7.

The actual stoichiometric weight percent added by the vendor has been shown by infrared measurements to be about 7.5%. Thus, B-staging by the vendor has reduced the amount of uncombined curing agent No. 2 to 4.3% in the as-received material. A plot of the concentration of the unreacted curing agent No. 2 vs in-house B-staging time is shown in Figure 6.

TABLE 6. EFFECT OF B-STAGING ON RHEOLOGY FOR ADHESIVE (TYPES I AND II)

Material	B-Stage Condition (hr @ 240°F)	RDS-Flow Number (min/Poise) x 10^{-2}	Minimum Viscosity (Poise) x 10^{2}
Adhesive (Type I)	As-Received	7.80 (7.923, 7.686)	3.18 (3.12, 3.24)
	0.5	6.41 (6.037, 6.787)	3.90 (4.07, 3.74)
	1.0	5.25 (5.443, 5.064)	4.85 (4.78, 4.91)
Adhesive (Type II)	As-Received	8.34 (8.303, 8.379)	3.55 (3.55, –)
	1.0	7.18 (7.320, 7.035)	4.09 (3.96, 4.22)
	2.0	3.59 (3.590, 3.598)	7.43 (7.68, 7.18)
	3.0	2.14 (2.049, 2.235)	11.37 (10.91, 11.83)

GP13-0422-6

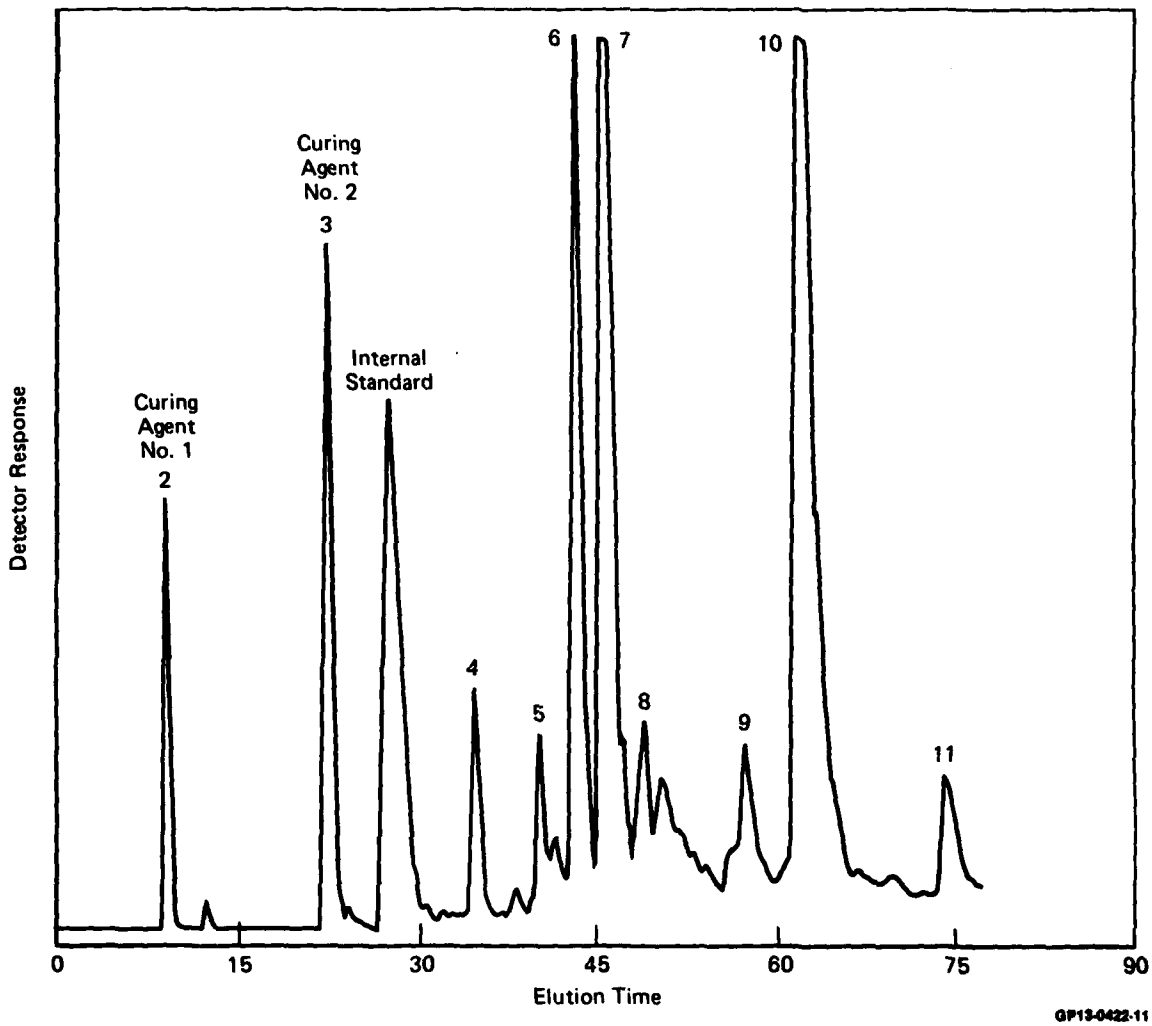


Figure 4. Separation of Adhesive Components by Liquid Chromatography (RPLLC)

Peak Number	Description of Reaction from FTIR Spectrum
1	TFH Solvent (Not Shown)
2	Curing Agent No. 1
3	Curing Agent No. 2
4	Undefined Polar Reaction Product of Curing Agent No. 2
5	Reaction Product of Curing Agent No. 2 and Epoxide No. 1 Resin
6	Epoxide No. 1 Resin
7	Intermediate Molecular Weight Epoxy Resin
8	Reaction Product of Curing Agent No. 2 and Epoxy Resin
9	Reaction Product of Curing Agent No. 2 and Epoxy Resin (Including Some Halogenated Epoxy Resin)
10	Reaction Product of Curing Agent No. 2 and Halogenated Epoxy Resin
11	Less Polar Reaction Product of Curing Agent No. 2 and Epoxy

GP13-0422-12

Figure 5. Identification of RPLLC Fractions

TABLE 7. EFFECT OF B-STAGING ON CHEMICAL AND THERMAL CHARACTERISTICS FOR ADHESIVE TYPE (II)

B-Stage Condition (hr @ 240°C)	Thermal Analysis DSC-2 @ 5°C/min		Concentration of Free Curing Agent No. 2 (wt/wt %) (1)
	On-Set Temperature (°C)	ΔH (Cal/g)	
As-Received	158.3	64.3	4.26 (4.28, 4.25)
1.0	157.1	59.4	1.62 (1.43, 1.82)
2.0	155.3	54.9	0.90 (0.83, 0.97)
3.0	151.5	49.8	0.44 (0.43, 0.44)

GP13-0422-6

Note:

(1) Film basis (includes scrim)

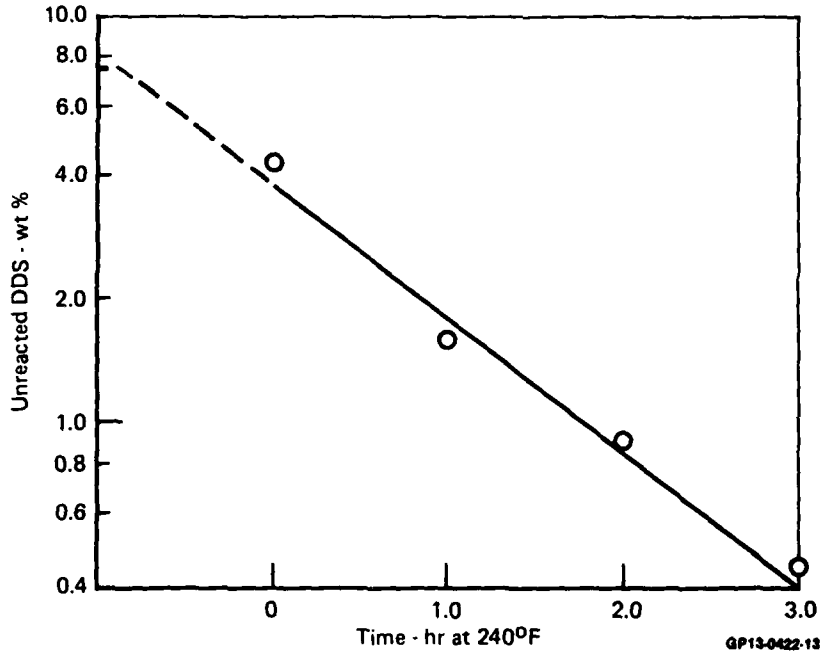


Figure 6. Effect of B-Staging on the Concentration of Unreacted Curing Agent No. 2

Thermal Characterization by Differential Scanning Calorimetry - Differential Scanning Calorimetry (DSC) was used for thermal analysis of the Type II adhesive batch in the as-received condition and after additional B-staging at 240°F for 1, 2, and 3 hours. The Perkin-Elmer Thermal Analysis Station was used. In the differential scanning calorimetry (DSC) mode, the instrument records the rate of energy released or absorbed as a function of temperature at a selected linear heating rate. The "thermal signature" obtained for thermosetting resins is used in routine quality control. A thermogram of the as-received adhesive Type II is shown in Figure 7. The on-set temperature and exopeak temperatures plus the exothermal heat of the cure reaction, obtained by integration of the cure reaction curve, are automatically calculated and recorded on the thermogram. The data is given is Table 7.

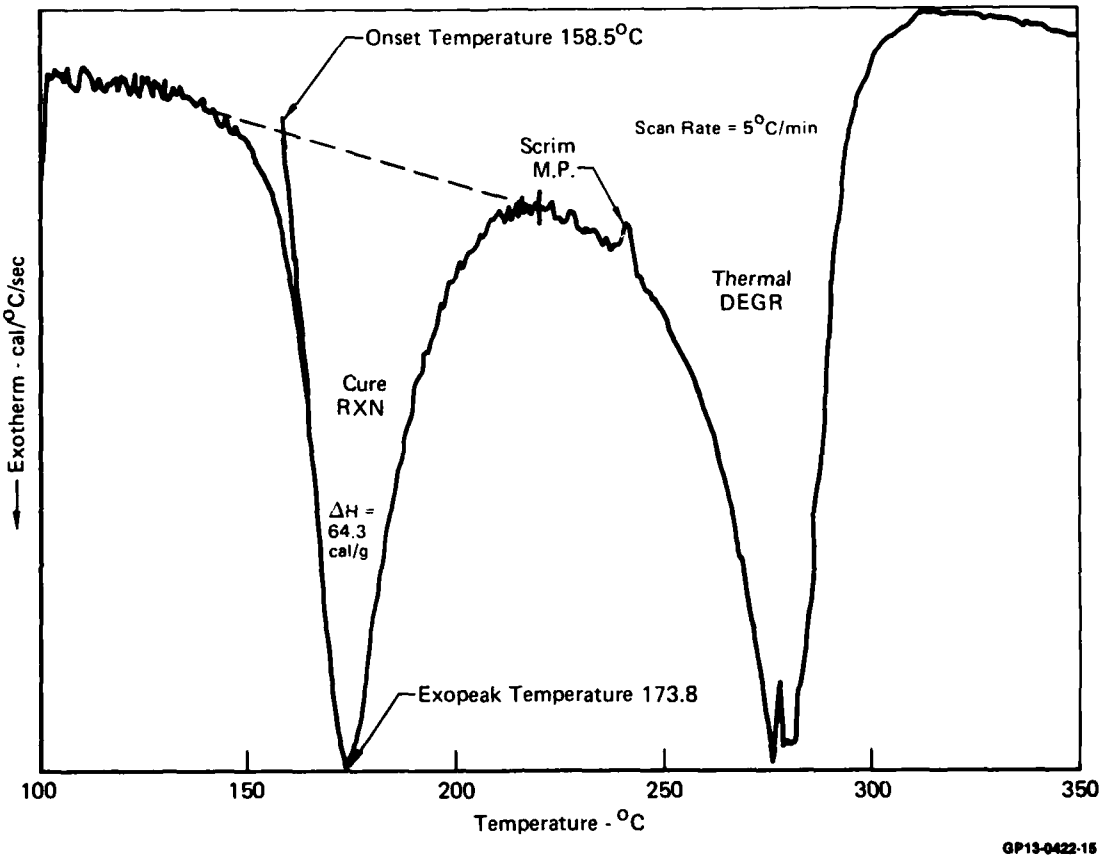


Figure 7. DSC Thermogram for Adhesive, Type II

3.3.3 Mechanical Properties of B-Staged Specimens - Bell peel and double lap shear specimens were fabricated from Type II adhesive in the as-received condition and from material staged 1, 2, and 3 hours at 240°F. Five specimens from each condition were tested at -65°F, RT, and 250°F. The data are given in Table 8.

For Bell peel, tests at 250°F showed improved peel strength for 1.0 and 2.0 hours B-staging. The test values for peel strength of -65°F and RT were inconclusive, and the -65°F peel strength values were all exceptionally low. For specimens tested at room temperature and 250°F the best double lap shear strength values were obtained for 2 hours B-staging. Strength at -65°F was not improved by B-staging.

TABLE 8. EFFECT OF B-STAGING ON MECHANICAL PROPERTIES FOR ADHESIVE, TYPE II

Bell Peel

B-Stage Condition (Hours @ 240°F)	Average Peel (lb/in.)(1)		
	−65°F	R.T.	250°F
As-Received	3.2	21.4	48.6
S_x	(1.1)	(8.3)	(6.4)
1	4.5	10.7	50.0
S_x	(1.9)	(4.7)	(0.9)
2	3.5	13.3	54.4
S_x	(0.6)	(7.5)	(4.2)
3	3.5	11.3	49.3
S_x	(0.6)	(8.1)	(1.7)

Double Lap Shear

B-Stage Condition (Hours @ 240°F)	Failing Stress (psi)(1)		
	−65°F	R.T.	250°F
As-Received	7,340	5,155	2,715
S_x	(899)	(345)	(116)
1	6,745	4,985	2,715
S_x	(132)	(190)	(235)
2	6,280	5,880	2,830
S_x	(304)	(379)	(304)
3	6,720	4,590	2,490
S_x	(488)	(473)	(182)

(1) Average of 5 values
(2) S_x = standard deviation

GP13-0422-18

3.3.4 Correlation of Data - The effect of variations in the B-staging of the adhesive can be quantitatively measured by both rheological and physiochemical methods. The amount of flow, as measured by the optimized RDS test method, shows a consistent decrease in flow with increased B-stage time. The minimum viscosity values are also consistent and the values increase with increased B-staging. The degree of advancement also correlates well with the amount of uncombined curing agent No. 2 as measured by liquid chromatography. Thermal analysis data shows a continuous decrease in onset temperature and heat of reaction with increased B-stage time. The rheological and physiochemical property measurement are sufficiently quantitative and precise for use in optimizing the mechanical properties.

3.4 PHASE IV - ESTABLISH RECEIVING INSPECTION CONTROLS FOR SYSTEM RHEOLOGY - The primary objective of this program was to establish receiving inspection controls that would ensure consistent rheological properties and response to cure for in-coming adhesive, Types I and II. In the course of our investigation, we compared rheological properties with physiochemical properties and found that the heat of reaction (ΔH) as determined by differential scanning calorimetry (DSC) measurements afforded a more meaningful control for thermal characteristics than did exotherm peak temperature (T_{exo}) originally proposed in Reference (1). Therefore, we have tested five production batches each of Type I and Type II adhesive for thermal characteristics as well as rheological properties.

3.4.1 Thermal Analytical Data - From the data given in Table 9, it is recommended that the heat of reaction (ΔH) be used for the thermal acceptance criteria to replace the current control based on T_{exo}.

3.4.2 Rheological Property Data - From the data given in Table 10, it is recommended that the RDS Flow Number be used for the rheological acceptance criterion. Analysis of variance showed that the optimized test procedure gave acceptable precision (repeatability) and that a large variation in batch-to-batch flow properties is responsible for the exceptionally large

TABLE 9. THERMAL ANALYSIS DATA FOR FIVE PRODUCTION BATCHES FOR ADHESIVE (TYPES I AND II)

Material	Batch Number	DSC-2 @ 10°C/min	
		On-Set Temperature (°C)	ΔH (Cal/g)
Adhesive (Type I)	374	165.8 (165.6, 166.0)	63.2 (63.5, 63.0)
	375	164.0 (164.1, 163.8)	69.0 (69.1, 69.0)
	376	165.0 (165.7, 164.4)	67.6 (65.7, 69.6)
	377	165.0 (164.9, 165.1)	63.0 (63.2, 62.7)
	380	163.3 (163.2, 163.4)	63.5 (62.8, 64.2)
Mean		164.6	65.3
Standard Deviation		1.0	2.9
"A" Allowable Range		164.6 ± 4.4	65.3 ± 12.7
Adhesive (Type II)	108	163.2 (162.8, 163.6)	68.8 (68.9, 68.8)
	113	166.2 (165.9, 166.4)	65.5 (65.5, –)
	115	164.6 (164.6, 164.5)	70.9 (71.0, 70.8)
	118	164.0 (163.9, 164.2)	71.0 (70.4, 71.5)
	120	165.2 (165.4, 165.0)	64.4 (64.0, 64.9)
Mean		164.6	68.4
Standard Deviation		1.1	2.9
"A" Allowable Range		164.6 ± 4.8	68.4 ± 13.3

GP13-0422-7

TABLE 10. RHEOMETRICS DATA FOR FIVE PRODUCTION BATCHES FOR ADHESIVE (TYPES I AND II)

Material	Batch Number	RDS Flow Number (min/Poise x 10^{-2})	Viscosity, η Minimum (Poise) x 10^2
Adhesive (Type I)	364	10.04 (9.779, 10,300)	2.62 (2.709, 2.540)
	375	10.26 (10.32, 10.19)	2.56 (2.566, 2.548)
	376	8.90 (8.645, 9.157)	3.01 (3.065, 2.960)
	377	8.97 (8.967, 8.967)	2.98 (3.004, 2.947)
	380	8.82 (9.053, 8.583)	2.90 (2.853, 2.946)
Mean		9.40	2.81
Standard Deviation		0.68	0.20
"A" Allowable Range		9.40 ± 3.01	2.81 ± 0.89
Adhesive (Type II)	108	8.36 (8.422, 8,307)	3.54 (3.526, 3.560)
	113	7.69 (8.034, 7.342)	3.79 (3.636, 3.940)
	115	12.90 (13.55, 12.26)	2.09 (1.972, 2.206*)
	118	10.51 (10.02, 11.00)	2.73 (2.778, 2.687)
	120	9.22 (9.111, 9.338)	3.05 (3.099, 3.008)
Mean		9.74	3.04
Standard Deviation		1.99	0.64
"A" Allowable Range		9.74 ± 8.84	3.04 ± 2.84

* Run 24 days later (> out time)

GP13-0422-8

standard deviation. Acceptance limits based on these data which would encompass 99% of the expected variation with 95% confidence ("A" allowable range) gives an unacceptably large spread. It is therefore recommended that the accept/reject limits be established after this variation is brought under control by the vendor and sufficient data is collected from future production batches.

4.0 CONCLUSIONS

Quantitative rheological control of as-received adhesives Types I and II can be achieved using the method developed in this program. It can be applied to the adhesives without separating the resin from supporting scrim. A computer program utilizing measured viscosity data can be used to give a quantitative measure for total resin flow under cure cycle conditions.

Variations in the moisture content of the adhesive, including equilibrium at 90% RH, have only a minor effect on the rheological and mechanical properties.

Variations in the degree of advancement or B-stage condition of the adhesive can be quantitatively measured by the optimized rheological test method. Total resin flow measurements correlate well with the concentration of free (uncombined) curing Agent No. 2, as measured by reverse phase liquid chromatography, and with the exothermal heat of the cure reaction as measured by differential scanning calorimetry. For the particular adhesive batch used for B-staging effect studies, the best peel and shear strength properties are obtained after two hours of additional in-house staging at 240°F.

While the rheological property data demonstrated good test method precision, the batch-to-batch variation was too great to establish meaningful accept/reject limits. It is recommended that acceptance limits be established at a later date after sufficient data is available from future production batches.

REFERENCE

1. Sewell, T.A., "Chemical Characterization and Quality Control for an Adhesive", LASC Contract No. N00019-79-C-0064, Final Report dated February 1981.

DISTRIBUTION LIST

Addressee	No. of Copies
Commander Naval Air Systems Command Dept. of the Navy Washington, DC 20361 Attn: Code AIR-5163D2	4
Commander Naval Air Systems Command Dept. of the Navy Washington, DC 20361 Attn: Code AIR-954	8
Commander Naval Air Systems Command Dept. of the Navy Washington, DC 20361 Attn: Code AIR-320A	1
Commander Naval Surface Weapons Center White Oak, Silver Spring, MD 20910 Attn: Dr. Joseph Augl (Code 234)	1
Air Force Materials Laboratory Wright-Patterson AFB, OH 45433 Attn: Codes MBC MXE LN LAE LT LAM	6
Director Plastics Technical Evaluation Center U.S. Army Armament Research & Development Center Dover, NJ 07801	1
Hercules Incorporated Magna, UT 84044 Attn: Mr. E. G. Crossland	1
TWR, Inc. One Space Park Rodundo Beach, CA 90278 Attn: R. W. Vaughn	1
University of Maryland College Park, MD 20742 Attn: Dr. W. J. Bailey	1

Addressee	No. of Copies
Naval Research Laboratory Washington, DC 20375 Attn: Dr. W. D. Bascom, Chemistry Div. (Code 6170)	1
North American Aviation Rockwell International Columbus Division 4300 E. Fifth Ave. Columbus, OH 43216	1
Commanding Officer Naval Air Development Center Warminster, PA 18974 Attn: Aero Materials Laboratory (Code 6060) (Structures Division)	1
Northrop Corporation 1001 E. Broadway Hawthorne, CA 90250 Attn: Technical Library	1
Lockheed California Co. Dept. 74-54, Bldg. 63 Box 551 Burbank, CA 91503 Attn: Mr. J. H. Wooley	1
Naval Research Laboratory Washington, DC 20350 Attn: Code 6120 (1 copy) Code 8433 (1 copy)	2
The Boeing Co. Aerospace Division P.O. Box 3707 Seattle, WA 98124 Attn: Library	1
Office of Naval Research Washington, DC 20361 Attn: Code 471	1
NASA Headquarters 600 Independence Ave., S.W. Washington, DC 20546 Attn: Library	1
Batelle Columbus Laboratories 505 King Ave. Columbus, OH 43201	1

Addressee	No. of Copies
Commander Naval Material Command Headquarters Washington, DC 20361 Attn: Code MAT 04H	1
Lockheed Missiles and Space Center Sunnyvale, CA 94088 Attn: Mr. Clayton May	1
Materials Engineering Laboratory U.S. Army Armament R&D Command Dover, NJ 07801 Attn: Mr. R. F. Wegman	1
National Academy of Science 2101 Constitution Ave., N.W. Washington, DC 20418 Attn: Dr. R. S. Shane, NMAB	1
Stanford Research Institute 333 Ravenswood Ave. Menlo Park, CA 94025 Attn: Mr. Milan Maximovich (1 copy) Technical Library (1 copy)	2
Commander Naval Ship Engineering Center National Center #2, Room 5E52 Washington, DC 20361 Attn: Mr. John Alfers	1
Commanding Officer Naval Air Rework Facility Naval Air Station Norfolk, VA 23511 Attn: Mr. Harold Sommerflek, Code 343	1
Commanding Officer Naval Air Rework Facility Naval Air Station Jacksonville, FL 32212 Attn: Code 343	1
Commanding Officer Naval Air Rework Facility Marine Corps Air Station Cherry Point, NC 28533 Attn: Mr. Fred Latham, Code 343	1

Addressee	No. of Copies
Commanding Officer Naval Air Rework Facility Naval Air Station Nroth Island, San Diego, CA 92123 Attn: Ms. Carol Duesler, Code 343	1
Commanding Officer Naval Air Rework Facility Naval Air Station Alameda, CA 94501 Attn; Mr. Norman Amdur, Code 343	1
Commanding Officer Naval Air Rework Facility Naval Air Station Pensacola, FL 32508 Attn: Mr. Faoro, Code 343	1
McDonnell Aircraft Company P.O. Box 516 St. Louis, MO 63166 Attn: Dr. James Carpenter, Dept. 347/B32/3	1
Grumman Aerospace Corp. Bethpage, NY 11714 Attn: Technical Library	1